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for

Network templated sequential assembly at the liquid/solid interface

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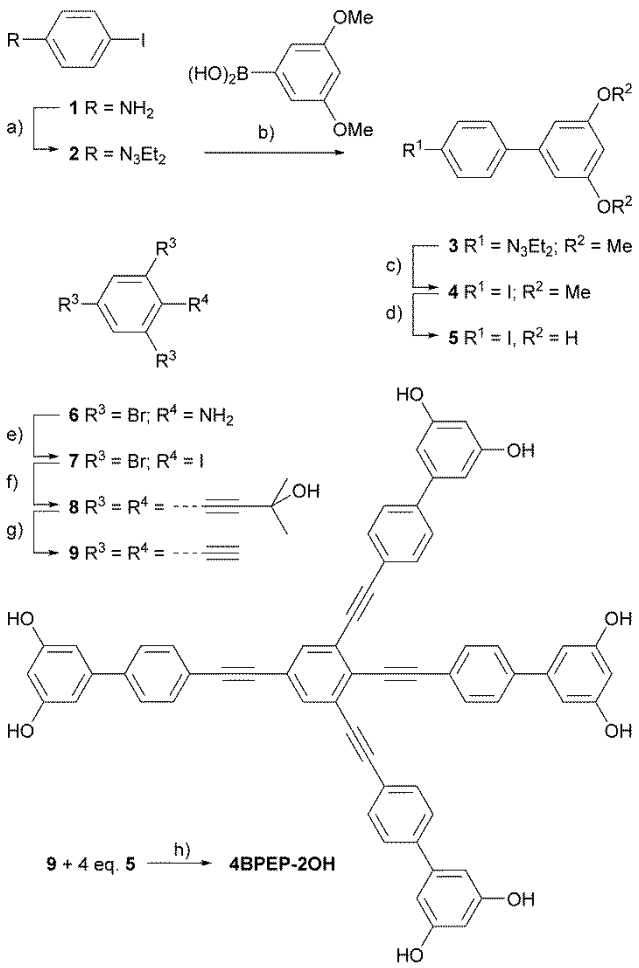
1. Synthesis of the four-armed star structure 4BPEB-2OH

The synthesis is displayed in S**cheme ESI 1**. The numbering of the structures corresponds to the one used in Scheme 1 of the main text. The assembly of the guest molecule **4BPEP-2OH** is based on Pd catalyzed cross-coupling chemistry. In a convergent synthetic strategy, all the four ethynyl groups exposed at the central building block 1,2,3,5-tetraethynylbenzene (**9**) were reacting with 4'-Iodo-[1,1'-biphenyl]-3,5-diol (**5**) in a *Sonogashira* reaction providing the desired four-armed star structure in 49% isolated yield after column chromatography.

The iodo-functionalized biphenyldiol **5** was assembled starting with 4-iodo aniline (**1**). First the amine functional group was transformed into a di-ethyl triazine acting as a "masked iodine". The di-ethyl triazine derivative **2** was isolated in 53% yield after column chromatography. The remaining iodine substituent of **2** was exposed to microwave *Suzuki* coupling conditions with 3,5-dimethoxyphenyl boronic acid providing the biphenyl derivate **3** in 56% yield. As side reaction causing the limitation in yield, the loss of the triazine functional group was identified. Functional group interconversion of the triazine to iodine was made by heating **3** in super heated MeI in a sealed tube to give the iodo-functionalized biphenyl **4** in good 90% isolated yield. Transformation of both methoxy groups of **4** to hydroxy groups worked almost quantitatively using BBr_3 in dichloromethane at low temperature. After warming to room temperature overnight the required biphenyl building block **5** was isolated in 97% yield.

As second building block the central 1,2,3,5-tetraethynylbenzene (**9**) was assembled. 1,3,5-tribromo-2-iodobenzene (**7**) was obtained in a one-pot *Sandmeyer* procedure from the commercially available 2,4,6-tribromoaniline (**6**). Applying *Sonogashira* coupling conditions, all four halides of **7** were substituted with 2-hydroxypropyl (HOP) protected acetylenes. It is noteworthy that initial approaches using trialkylsilyl protected (TIPS and TMS) acetylenes failed to substitute all four halogen atoms. The fourfold HOP-ethynyl functionalized benzene **8** was isolated in acceptable 49% yield. The four ethynyl groups were liberated in a retro-Favorskii reaction by treatment with sodium hydride in refluxing toluene. The required 1,2,3,5-tetraethynylbenzene (**9**) was isolated by column chromatography in 49% and used immediately after its isolation.



Scheme ESI 1: Synthesis of the four-armed star structure **4BPEB-2OH**. Reagents and conditions: a) conc. HCl, aq. $NaNO_2$, Et_2NH, K_2CO_3, 0°C to RT., 53%; b) $Pd(PPh_3)_2Cl_2$, K_2CO_3, $C_6H_5CH_3$, EtOH, MicroWave, 120°C, 45 min., 56%; c) MeI, 130°C, 90%; d) BBr_3, CH_2Cl_2, -78°C to RT., 97%; e) 1.) $pTsOH{\cdot}H_2O$, $NaNO_2$, KI, CH_3CN, H_2O, 15˚C, 10 min.; 2.) 20˚C, 2h, 68%; f) 2-methyl-3-butyn-2-ol, $Pd(PPh_3)_2Cl_2$, CuI, DMF, Et_2NH, 80˚C, 24h, 49%; g) NaH, $C_6H_5CH_3$, 120˚C, 3h, 49%; h) $Pd(PPh_3)_4$, CuI, THF, *i*Pr_2NH, 45˚C, 16h, 45%.

Experimental Part

General Remarks: All commercially available starting materials were of reagent grade and used as received. Analytical thin layer chromatography (TLC) was carried out on Merck silicagel 60 F254 glass TLC plates visualizing with UV light at 254 nm and 366 nm. Column chromatography was performed using silica gel 60 (230-240 mesh), except were stated otherwise. Deuterated solvents were purchased from Cambridge Isotope Laboratories. ^1H and ^{13}C NMR spectra were recorded with a *Bruker* DMX 400 instrument (^1H resonance 400 MHz, ^{13}C resonance 101 MHz) or a *Bruker* DRX 500 instrument (^1H resonance 500 MHz, ^{13}C resonance 125 MHz) at 298 K. Chemical shifts (δ) are quoted in parts per million (ppm) relative to the residual solvent proton peak ($CDCl_3$: 7.26 ppm) and solvent residual carbon peak ($CDCl_3$, δ = 77.16.) Multiplicities are denoted; singlet (s), doublet (d), triplet (t), multiple (m) and doublet of doublets (dd). Mass spectra were obtained by GC-MS recorded on a Shimadzu GCMS-QP2010

SE gas chromatography system. For high resolution mass spectrometry (HRMS) a HR-ESI-ToF-MS measurement was performed on a *maXis*^{TM} *4G* instrument from *Bruker* measured by Dr. H. Nadig. Molecular ions are denoted and only the major peak reported. Elemental analyses (EA) were measured by W. Kirsch on a Perkin-Elmer Analysator 240 and the values are given in percent.

3,3-diethyl-1-(4-iodophenyl)triaz-1-ene (2): To a suspension of 4-iodoaniline (4.00 g, 18.3 mmol) in concentrated hydrochloric acid (35%, 26 mL) was added a solution of $NaNO_2$ (1.39 g 20.1 mmol) in water (6 mL) at 0°C. After stirring at 0°C for 30 min, the resulting mixture was slowly added dropwise to a suspension of K_2CO_3 (20.4 g, 146 mmol), diethylamine (17 mL), and water (80 mL) at 0°C. The reaction mixture was then warmed to room temperature and stirred for 1 h. After extraction with ethyl acetate, the organic layer was evaporated, and the residue was passed through a column (1:1 cyclohexane/DCM), fractions combined and solvent removed to afford **2** as a red oil (2.92 g, 9.63 mmol, 53%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ_H = 7.64 – 7.59 (m, 2H), 7.19 – 7.13 (m, 2H), 3.75 (q, *J* = 7.2 Hz, 4H), 1.26 (t, *J* = 6.4 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ_C = 151.0, 137.8, 122.6, 89.1. **GC-MS** *m*/*z*; 304 $[M+H]^{\cdot +}$.

1-(3',5'-dimethoxy-[1,1'-biphenyl]-4-yl)-3,3-diethyltriaz-1-ene (3): A microwave vial was charged with **2** (1.11 g, 3.68 mmol), $PdCl_2(PPh_3)_2$ (261 mg, 368 µmol), K_2CO_3 (1.54 g, 11.0 mmol) and 3,5-dimethoxyphenylboronic acid (0.704 g, 3.68 mmol) dissolved in a degassed mixture of toluene (10 mL) and EtOH (5 mL). The MW vial was sealed and irradiated in the MW (5 min pre-stirring, normal absorbance, 45 min at 120°C). Then the mixture was poured into water, and extracted with TBME. The organic layer was washed with 2M HCl (aq), brine and dried over $MgSO_4$. The crude was passed through a column of SiO_2 (1/1 cyclohexane-DCM), fractions combined and solvent removed to afford **3** as a yellow oil (640 mg, 2.04 mmol, 56%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ_H = 7.55 (dd, *J* = 8.3, 2.0 Hz, 2H), 7.47 (dd, *J* = 8.4, 2.1 Hz, 2H), 6.75 (t, *J* = 2.4 Hz, 2H), 6.44 (d, *J* = 2.3 Hz, 1H), 3.86 – 3.84 (m, 6H), 3.78 (dt, *J* = 6.6, 5.8 Hz, 4H), 1.28 (t, *J* = 6.8 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ_C = 161.1, 151.0, 143.5, 137.8, 127.7, 120.8, 105.3, 99.1, 55.6.

4'-iodo-3,5-dimethoxy-1,1'-biphenyl (4): A 5 mL sealed tube was charged with **3** (388 mg, 1.24 mmol) using DCM to transfer this oil, the solvent was evaporated and then **3** was dissolved in MeI (3 mL) the tube sealed and heated to 130°C overnight. Then the MeI was distilled off inside a fume hood, and the crude left behind passed through a short column on SiO_2, fractions evaporated to afford **4** as a dark oil (378 mg, 1.11 mmol, 90%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ_H = 7.74 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 6.67 (d, *J* = 2.1 Hz, 2H), 6.47 (t, *J* = 2.1 Hz, 1H), 3.83 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ_C = 161.3, 142.4, 140.8, 137.9, 129.1, 105.4, 99.7, 93.4, 55.6.

4'-iodo-[1,1'-biphenyl]-3,5-diol (5): A 100 mL round bottom flask was charged with **4** (480 mg, 1.41 mmol) dissolved in dry DCM (30 mL) under argon. The solution was cooled to –78°C and then BBr_3 (1M solution in DCM, 10 mL, 10 mmol) was added dropwise by a syringe. The reaction was left stirring to warm overnight. The reaction was quenched by the slow addition of water, followed by extraction with DCM. The organic phase was washed and dried over $MgSO_4$. The crude was passed through a column of SiO_2 (1:1 cylclohexane:EtOAc), fractions combined and solvent removed to afford **5** as a colourless oil (427 mg, 1.37 mmol, 97%). **NMR** (400 MHz, CD_3CN): δ_H = 7.79 – 7.71 (m, 2H), 7.38 – 7.29 (m, 2H), 7.04 (s, 2H), 6.56 (d, *J* = 2.2 Hz, 2H),

6.31 (t, *J* = 2.2 Hz, 1H). **^{13}C NMR** (101 MHz, CD_3CN): δ_C = 159.4, 143.0, 141.3, 138.7, 129.8, 106.5, 102.8, 93.5.**^{1}H NMR** (400 MHz, MeOD): δ_H = 7.74 – 7.68 (m, 2H), 7.33 – 7.27 (m, 2H), 6.52 (d, *J* = 2.2 Hz, 2H), 6.29 (t, *J* = 2.2 Hz, 1H). **^{13}C NMR** (101 MHz, MeOD): δ_C = 160.0, 143.3, 142.1, 138.8, 129.8, 106.3, 102.9, 93.4. **MS** (EI +, 70 eV) *m*/*z* (%) = 312.0 (100) [M^+]. **GC-MS** *m*/*z*; 12.91 min, 314 [M]$^{\cdot+}$ **Anal.** Calcd for $C_{12}H_9IO_2$: C, 46.18; H, 2.91. Found: C, 46.34; H, 3.06.

1,3,5-tribromo-2-iodobenzene (7): To a solution of pTsOH·H_2O (35 g, 182 mmol) in MeCN (240 mL) in a two necked 1L flask 2,4,6-tribromoaniline (20 g, 61 mmol) was added. The resulting suspension of amine salt was cooled to 5-10˚C and to this was added, gradually via a dropping funnel, a solution of $NaNO_2$ (8.37 g, 121 mmol) and KI (25 g, 152 mmol) in water (36 mL). The reaction mixture was stirred for 10 min at this temperature and then allowed to reach 20˚C and stirred again for 2h. The reaction mixture was then basified with a solution of $NaHCO_3$ (1M, until pH=9-10) and extracted with TBME (3x). The combined organic layers were then washed with a solution of $Na_2S_2O_3$ (20% aq.), washed with water (until neutral pH), dried over Na_2SO_4, filtered and evaporated. The rest of the crude (23.71 g, dark brown solid) was recrystallized in EtOH (200 mL) giving the desired compound **7** as brown needles (18.2 g, 41.3 mmol, 68%). **TLC** (SiO_2, hexane): R_f = 0.4, **^{1}H NMR** ($CDCl_3$, 400 MHz) δ_H: 7.70 (s, 2H, CH). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ_C: 133.6 (CH, 2C), 131.8 (Cq, 2C), 123.0 (CH, 1C), 108.1 (CH, 1C).

1,2,3,5-tetra(3-hydroxy-3-methylbut-1-yn-1-yl)benzene (8): A flame dried 250 ml two necked flask was flooded with argon and charged with **7** (4.0 g, 9.08 mmol) in DMF (40 mL) containing *i*Pr_2NH (4 mL). The solution was bubbled with argon for 10 minutes. 2-methylbut-3-yn-2-ol (9.16 g, 109 mmol) was added and bubbled with argon for another 5 minutes. $Pd(PPh_3)_4$ (319 mg, 0.454 mmol) and CuI (86 mg, 0.454 mmol) were added and the reaction mixtures was stirred at 80°C for 24h. After aqueous work up the crude reaction mixture was chromatographed (silica gel, CH_2Cl_2/EtOAc 6:4) giving the desired product **8** (1.8 g, 4.43 mmol, 49%). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ_H: 7.30 (s, 2H, CH), 1.64 (s, 6H, CH3). 1.61 (s, 12H, CH3). 1.58 (s, 6H, CH3). ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C: 133.7 (CH, 2C), 127.3 (Cq, 1C), 125.6 (Cq, 2C), 122.2 (Cq, 1C), 103.6 (Cq, 1C), 98.7 (Cq, 2C), 96.3 (Cq, 1C), 80.3 (Cq, 1C), 79.7 (Cq, 2C), 79.4 (Cq, 1C), 65.6 (Cq, 1C), 65.4 (CH, 2C), 65.3 (Cq, 1C), 31.4 (CH, 2C), 31.4 (CH, 4C), 31.3 (CH, 2C).

1,2,3,5-tetraethynylbenzene (9): Compound **8** (440 mg, 1.08 mmol) was dissolved in dry toluene and this solution was degassed for 10 min. Sodium hydride (173 mg, 4.33 mmol, 60% dispersion in oil) was added and the reaction mixture was stirred at 120˚C for 3h. The reaction mixture was poured on a silica plug, eluted with CH_2Cl_2 giving the crude mixture which was then chromatographed (silica gel, CH_2Cl_2/cyclohexane 1:2) giving the desired product **9** as a yellow solid (92 mg, 0.528 mmol, 49%). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ_H: 7.60 (s, 2H, CH), 3.67 (s, 1H, CH), 3.36 (s, 2H, CH), 3.19 (s, 1H, CH).

1,2,3,5-tetra((3',5'-dihydroxy-[1,1'-biphenyl]-4-yl)ethynyl)benzene (4BPEB-2OH): A flame dried 100 ml two necked flask was flooded with argon and charged with **5** (264 mg, 0.846 mmol) in THF (20 mL) containing *i*Pr_2NH (2 mL). The solution was bubbled with argon for 10 minutes. 1,2,3,5tTetraethynylbenzene **9** (37 mg, 0.211 mmol) was added and bubbled with argon for another 5 minutes. $Pd(PPh_3)_4$ (24 mg, 0.021 mmol) and CuI (2.0 mg, 0.0106 mmol) were added and the reaction mixtures was stirred at 45°C overnight (ca. 16h). After aqueous work up the crude reaction mixture was chromatographed (reverse phase column (C18 40-60 RP-silica),

MeOH/H_2O 9/1) giving the desired product **4BPEB-2OH** as brown solid (86 mg, 0.094 mmol, 45%). **^{1}H NMR** (MeOD, 500 MHz) δ_H: 7.49-7.58 (m, 14H, CH), 7.44 (m, 3H, CH), 7.42 (m, 1H, CH), 6.62 (t, 4JHH=2.0 Hz, 8H, CH), 6.35 (m, 4H, CH), 5.11 (br s, 8H, OH). **^{13}C NMR** (MeOD, 125 MHz) δ_C: 158.6 (CH, 8C), 142.3 (Cq, 1C), 142.2 (Cq, 3C), 141.4 (Cq, 1C), 141.4 (Cq, 2C), 141.3 (Cq, 1C), 133.4 (CH, 2C), 131.9 (CH, 8C), 127.3 (Cq, 1C), 126.6 (CH, 8C), 126.4 (Cq, 2C), 122.9 (Cq, 1C), 122.1 (Cq, 1C), 121.8 (Cq, 2C), 121.4 (Cq, 1C), 105.4 (CH, 8C), 101.8 (CH, 3C), 99.2 (Cq, 1C), 94.1 (Cq, 2C), 91.7 (Cq, 1C), 88.2 (Cq, 1C), 88.1 (Cq, 1C), 88.0 (Cq, 2C). **HRMS** (ESI-ToF, *negative*)**:** calc. for $C_{62}H_{38}O_8$: 909.2494 $[M-H]^-$, found: 909.2497; 454.1211 $[M-2H]^{2-}$, found: 454.1214.

2. Additional STM images:

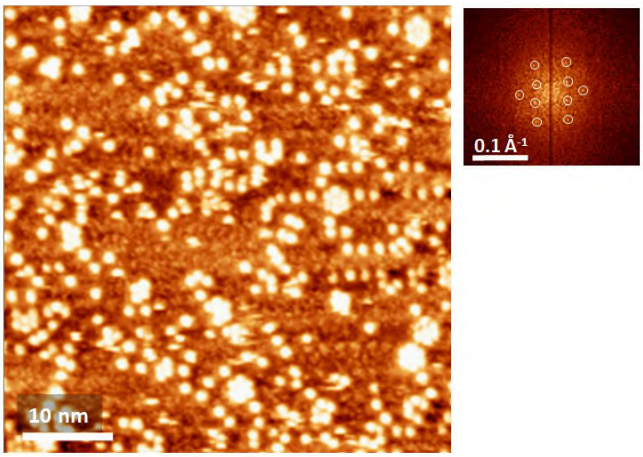


Fig. ESI1 (a) STM image of a 4BPEB-2OH modified PTCDI-melamine network on Au(111)/mica after immersion in a solution of C_{60} in 1,2,4-trichlorobenzene at a temperature of 60°C and an immersion time of 2 min. Diffraction spots in the Fourier transform are encircled.

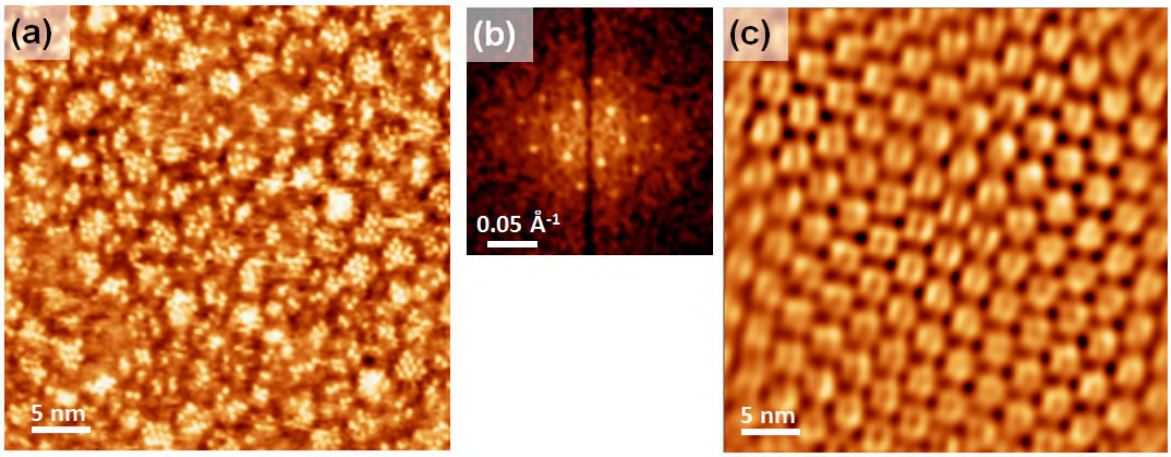


Fig. ESI2 (a) STM image of a 3BPEP-OH modified PTCDI-melamine network on Au(111)/mica after immersion in a 10 µM solution of adamantane thiol in ethanol at the melting temperature of the solution (~ -114°C) and an immersion time of 45s. Fourier transform and Fourier filtered image of (a) shown in (b) and (c), respectively.